NIWA Taihoro Nukurangi

Supplementary Information:

Comparison of ecotoxicology and environmental fate of metsulfuron methyl, haloxyfop-R-methyl, imazapyr isopropylamine and triclopyr TEA with glyphosate

In New Zealand, the herbicide glyphosate isopropylamine is registered for use in situations where contamination of aquatic environments may occur and is currently used to control a wide range of wetland and emergent aquatic weeds. Unfortunately, this herbicide does not give effective control of a range of problem weed species targeted for eradication including alligator weed, Manchurian wild rice, phragmites, purple loosestrife, sagittaria, Senegal tea and spartina. The major drive for seeking permission for the restricted use of metsulfuron methyl, haloxyfop methyl, imazapyr isopropylamine and triclopyr TEA is to allow for effective management of these species in eradication programmes.

This paper summarises data on ecotoxicology and environmental fate of glyphosate isopropylamine as a comparison with herbicides that contain metsulfuron methyl, haloxyfop methyl, imazapyr isopropylamine and triclopyr TEA, as evaluated in Champion (2012).

1 Glyphosate isopropylamine

A range of products with the active ingredient glyphosate isopropylamine are registered to be used in situations where contamination of aquatic environments may occur in New Zealand. In most instances, the use of this herbicide in these environments is not subject to resource consent requirements.

Twenty three products with 360 g/L a.i. glyphosate isopropylamine as a soluble concentrate are currently available under various trade names, with all but one product recommended for use in aquatic areas (New Zealand Novachem Manual 2012). There are additional products with 450, 510 and 540 g/L a.i. (6, 5 and 3 products respectively) (New Zealand Novachem Manual 2012). Only 540 g/L a.i. formulations recommend “avoid unintentional contamination of aquatic environments” (New Zealand Novachem Manual 2012).

1.1 Toxicology

The label for all formulations of glyphosate isopropylamine states that those products are ecotoxic, being toxic to aquatic organisms with long lasting effects (New Zealand Novachem Manual 2012).

At the rates recommended for application to aquatic plant pests (willow, floating and reed sweet grasses, Mercer grass, cutty grass and rushes) the maximum concentration of glyphosate isopropylamine in the spray mix applied to plants would be 8.1 g/L (or mg/kg) based on a rate of 9 L of the 360g/L a.i. applied per hectare.

The following literature has been used to generate the summary below: Peterson et al. (1994); EXTOXNET (1996); Monheit (2002); Solomon & Thompson (2003); Tsui & Chu

(2003) and factsheets from European Glyphosate Environmental Information Source (EGEIS) and National Pesticide Information Center (NPIS).

Mammalian toxicity

Very low toxicity

Acute oral toxicity that causes mortality (Lethal Dose) in half of the test animals (rats) (LD_{50}) >5000 mg/kg.

Glyphosate is poorly absorbed from the digestive tract and is largely excreted unchanged by mammals.

Avian toxicity

Very low toxicity

Acute oral toxicity - mallard (LD_{50}) > 5000 mg/kg.

Aquatic animal toxicity

Very low toxicity

96-hour (Lethal Concentration) LC_{50} – rainbow trout and bluegill sunfish 180 mg/L.

48-hour LC_{50} – *Daphnia magna* (cladoceran crustacean) 930 mg/L.

Solomon & Thompson (2003) concluded that the ecological risk assessment for aquatic organisms from the application of glyphosate over water at rates less than 4 kg/ha (rate used in New Zealand is 3.24 kg/ha) is of negligible or low risk.

Non-target aquatic plant toxicity

Very toxic

Glyphosate isopropylamine is less selective than any of the four herbicides assessed by Champion (2012). It is currently used to control a range of emergent (plants with foliage above the water level) plants e.g., willow, floating and reed sweet grasses, Mercer grass, cutty grass (*Carex* spp.) and rushes (New Zealand Novachem Manual 2012).

Peterson et al. (1994) showed no observable toxic effect of glyphosate in field trials on the floating *Lemna minor* at expected environmental concentrations resulting from herbicide application. EGEIS report a 1.5 mg/L LC_{50} for this species.

Algae

Selectively very toxic

Ecotoxicology studies using a range of algal species have found toxicity ranging from moderate to highly toxic (Peterson et al. (1994); Tsui & Chu (2003)).

Tsui & Chu (2003) found the green alga *Pseudokirchneriella subcapitata* was the least sensitive of species tested with an IC_{50} (inhibition coefficient) of 41 mg/L of glyphosate isopropylamine. The diatom *Skeletonema costatum* was more sensitive with an IC_{50} of 5.89 mg/L. This sensitivity of diatoms to glyphosate was also reported by Peterson et al. (1994)

with a 73 to 77% reduction at expected environmental concentrations resulting from herbicide application, whereas green algae were reduced by 3 to 18% under the same concentration.

1.2 Persistence in aquatic habitats

EXTOXNET (1996) report half-life of glyphosate in pond water from 12 to 70 days. Peterson et al. (1994) report a half-life of 47 days in their study. Glyphosate is very rapidly adsorbed by organic or mineral suspended solids and degradation is by microbial activity.

2 Comparison with metsulfuron methyl, haloxyfop-R-methyl, imazapyr isopropylamine and triclopyr TEA

The tables below summarise the persistence of these herbicides in aquatic environments and toxicity to non-target aquatic organisms:

Table 1. Chemical persistence in aquatic environments.

Agrichemcial	Half-life (days)	Breakdown method	Notes
Haloxyfop-R-methyl	5 – 33	Hydrolysis	Half-life dependant on pH of water. 5 days @ pH 7, several hours @ pH 9.
Imazapyr isopropylamine	2.5 – 5.3	Photolysis	
Metsulfuron methyl	5 – > 90	Hydrolysis under acid conditions	Half-life dependant on water pH and initial chemical concentration.
Triclopyr triethylamine	0.5 – 7.5	Photolysis	
Glyphosate isopropylamine	12 – 70	Metabolised by microorganisms	Strongly adsorbed to suspended organic and mineral matter.

Table 2. Toxicity of chemicals on selected aquatic species.

	Glyphosate isopropylamine	Haloxyfop-R-methyl	Metsulfuron methyl	Imazapyr propylamine	Triclopyr triethylamine
Application Rate (mg/L)	**810**	**750**	**150**	**250**	**792**
Rats LD_{50}	>5000	393	>5000	>5000	2574
Mallard LD_{50}	>4500	>5000	>5000	>5000	10000
Rainbow Trout LC_{50}	180	>800	>150	>800	552
Fathead Minnow LC_{50}	97	1000	-	-	101-120
Bluegill Sunfish LC_{50}	180	548	>150	>1000	552
***Daphnia* LC_{50}**	930	96.4	150	614	110
Green alga *Pseudokirchneriella subcapitata* IC_{50}	5.56	24.7	1.08	11.5	10.6
Other algae	Most toxic to diatoms	Possibly very toxic	Most toxic to cyanobacteria	Low toxicity	Moderately toxic
Selectivity of plant control	Non-selective	Grasses only	Some selectivity – grasses, sedges and rushes tolerant	Non-selective	Dicot selective

3 Summary

- Glyphosate isopropylamine has a longer half-life than haloxyfop methyl, imazapyr isopropylamine and triclopyr TEA. Metsulfuron methyl is stable under neutral or alkaline conditions, but breaks down rapidly under acid conditions.
- Glyphosate isopropylamine is applied at similar concentrations to haloxyfop methyl, and triclopyr TEA, but higher than metsulfuron methyl and imazapyr isopropylamine
- Glyphosate isopropylamine has similar mammalian and avian toxicity to metsulfuron methyl, imazapyr isopropylamine and triclopyr TEA. Haloxyfop methyl is more toxic to mammals.
- Glyphosate isopropylamine has similar or higher fish toxicity than metsulfuron methyl, haloxyfop methyl, imazapyr isopropylamine and triclopyr TEA.
- Glyphosate isopropylamine is less toxic to *Daphnia* than metsulfuron methyl, haloxyfop methyl, imazapyr isopropylamine and triclopyr TEA.

- Glyphosate isopropylamine has higher toxicity to the green alga *Pseudokirchneriella subcapitata* than metsulfuron methyl, imazapyr isopropylamine and triclopyr TEA, but less than haloxyfop methyl.
- Glyphosate isopropylamine has less selectivity to non-target angiosperms than metsulfuron methyl, haloxyfop methyl and triclopyr TEA, but similar to imazapyr isopropylamine.
- Glyphosate isopropylamine does not adequately control alligator weed, Manchurian wild rice, phragmites, purple loosestrife, sagittaria, Senegal tea and spartina.

4 Acknowledgements

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5 References

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